

Hexagonal Petals-like Cobalt Oxide Nanowire Arrays Encapsulated by MOF-derived Co/N-codoped Carbon for Boosting Electrochemical Capacitor Behaviour

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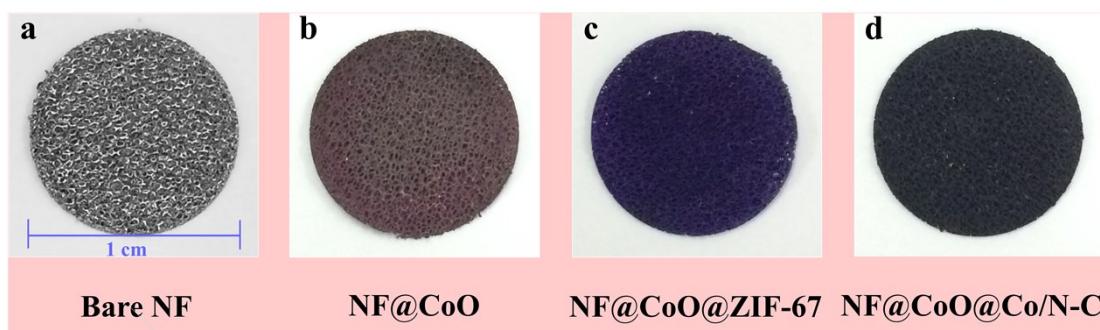


Figure S1. Photographs of the bare NF, NF@CoO, NF@CoO@ZIF-67 and NF@CoO@Co/N-C samples.

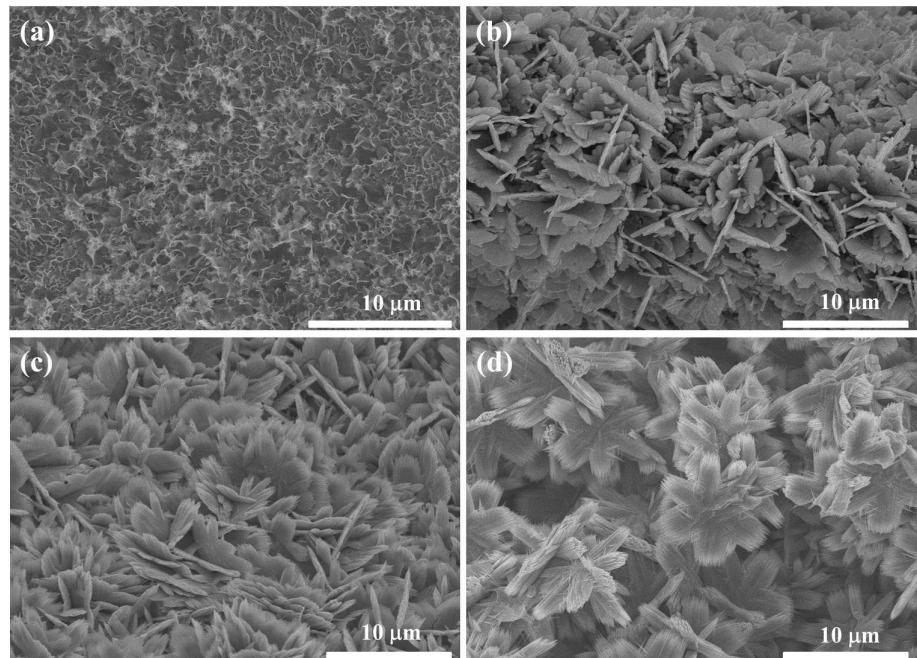


Figure S2. Formation process of nanowire-assembled hexagonal petals-like CoO. SEM images of CoO prepared at different reaction time length: (a) 10 min; (b) 1 h; (c) 5h; (d) 10 h.

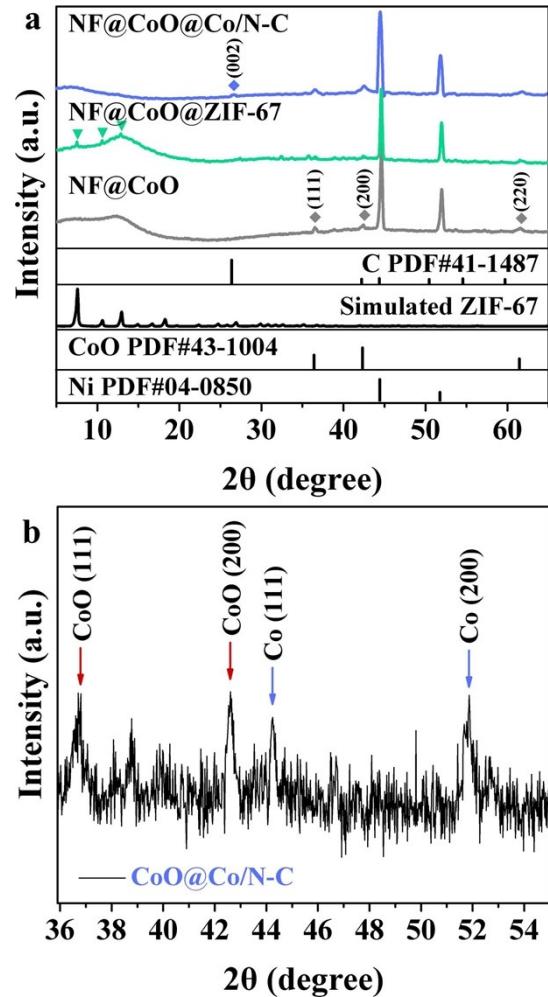


Figure S3. (a) PXRD patterns of NF@CoO, NF@CoO@ZIF-67 and NF@CoO@Co/N-C, (b) the enlarged PXRD pattern of CoO@Co/N-C powder sample without nickle foam.

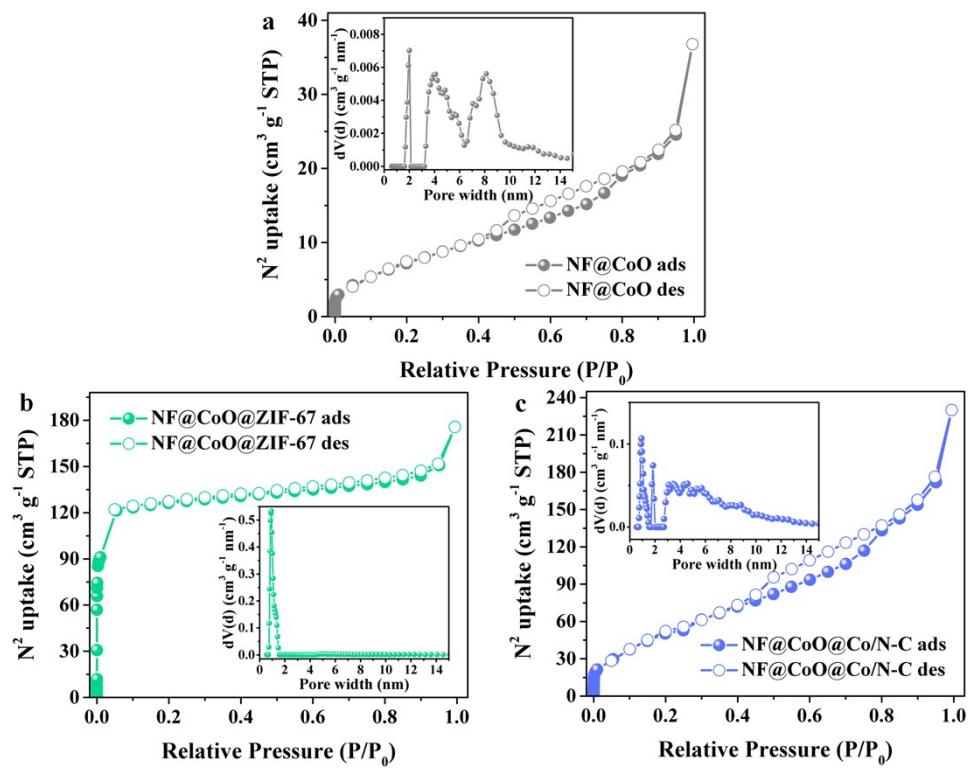


Figure S4. Nitrogen (77K) adsorption-desorption isotherms and pore size distribution for NF@CoO, NF@CoO@ZIF-67 and NF@CoO@Co/N-C.

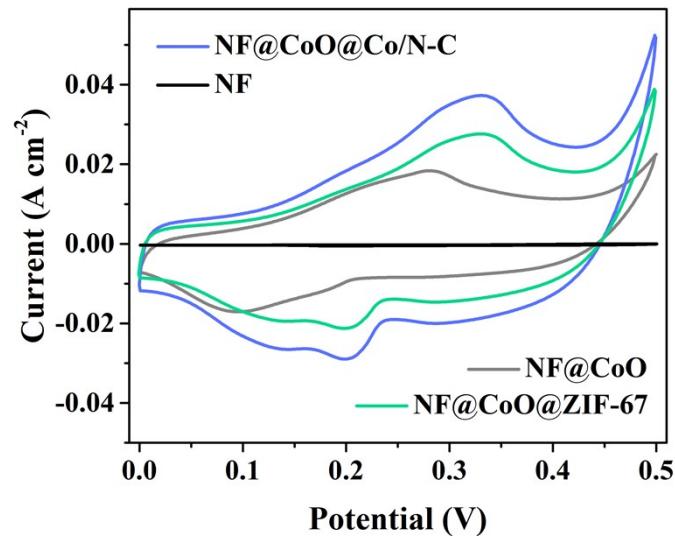


Figure S5. Cyclic voltammograms of bare NF, NF@CoO, NF@CoO@ZIF-67 and NF@CoO@Co/N-C at scan rate of 6 mV s^{-1} .

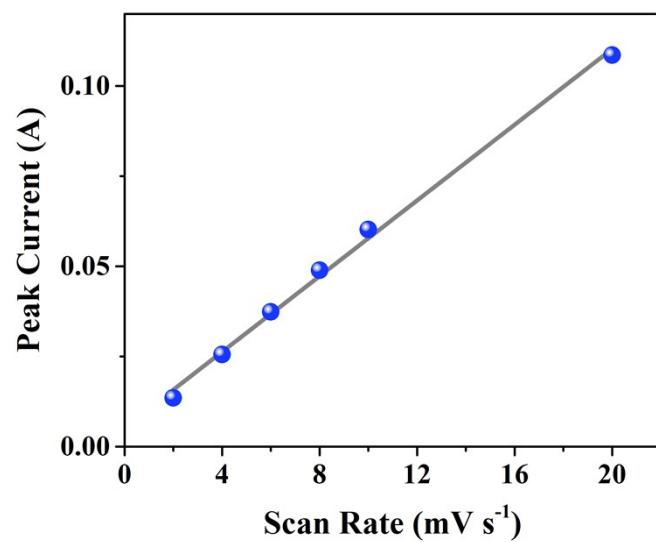


Figure S6. Relationship between anodic peak current and scan rate for NF@CoO@Co/N-C.

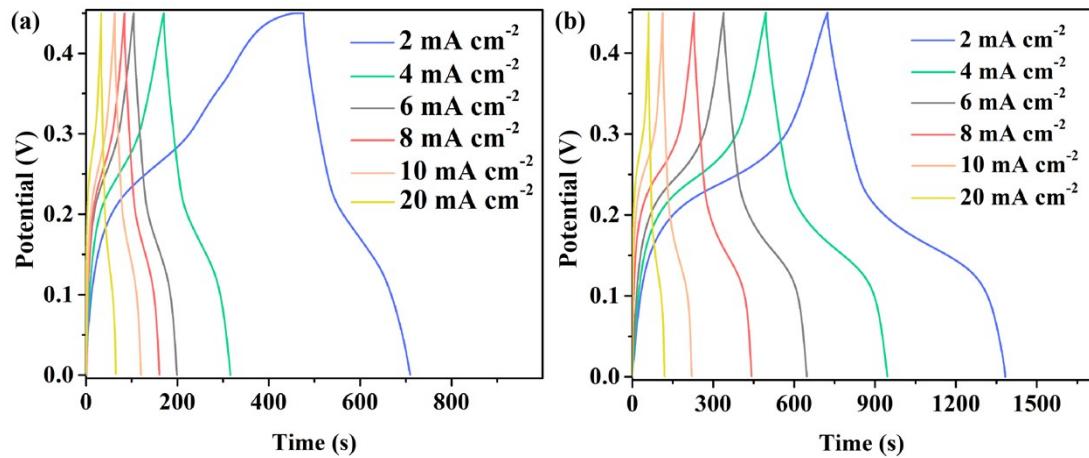


Figure S7. GCD curves recorded at different current densities from 2 to 20 mA cm⁻² for (a) NF@CoO, (b) NF@CoO@ZIF-67.

Table S1. Comparison of capacitance and rate capability of NF@CoO@Co/N-C with recently reported cobaltous oxide-based electrodes.

Electrode	Current density/ Scan rate	Electrolyte	Capacitance	Rate capability
CoO ^{S1}	0.5 A g ⁻¹	1 M KOH	600 F g ⁻¹	0.5~16 A g ⁻¹ (32 times) 69.3%
Co ₃ O ₄ @CoO@carbon ^{S2}	1 A g ⁻¹	1 M KOH	324 F g ⁻¹	1~10 A g ⁻¹ (10 times) 63. 9%
Co ₃ O ₄ @CoO ^{S3}	0.2 A g ⁻¹	6 M KOH	362.8 F g ⁻¹	0.2~4 A g ⁻¹ (20 times) 78.7%
Co ₃ O ₄ @CoO@Co@C ^{S4}	2 A g ⁻¹	1 M KOH	370 F g ⁻¹	1~40 mV s ⁻¹ (40 times) 64%
CoO/Co ₉ S ₈ @CN ^{S5}	0.5 A g ⁻¹	6 M KOH	303.3 F g ⁻¹	0.5~5 A g ⁻¹ (10 times) 70.0%
CoCO ₃ @CoO ^{S6}	1 A g ⁻¹	1 M KOH	0.77 F cm ⁻²	0.2~10 A g ⁻¹ (50 times) 82.0%
			510 F g ⁻¹	
CoO nanowall ^{S7}	1 A g ⁻¹	6 M KOH	352 F g ⁻¹	1~20 A g ⁻¹ (20 times) 72.7%
CoO@MnO ₂ ^{S8}	2 mA cm ⁻²	6 M KOH	2.40 F cm ⁻²	2~20 mA cm ⁻² (10 times) 57.5%
C/CoO-200 ^{S9}	0.5 A g ⁻¹	2 M KOH	207 F g ⁻¹	0.5~10 A g ⁻¹ (20 times) 79.6%
CoO@MnO ₂ NNAs ^{S10}	2 mA cm ⁻²	6 M KOH	3.03 F cm ⁻²	2~20 mA cm ⁻² (20 times) 46.9%
NF@CoO*	2 mA cm⁻²	6 M KOH	2.32 F cm⁻²	2~20 mA cm⁻² (10 times) 52.2%
NF@CoO@ZIF-67*	2 mA cm⁻²	6 M KOH	3.13 F cm⁻²	2~20 mA cm⁻² (10 times) 71.2%
NF@CoO@Co/N-C*	2 mA cm⁻²	6 M KOH	5.61 F cm⁻²	2~20 mA cm⁻² (10 times) 91.3%
			1693.4 F g⁻¹	

*This work

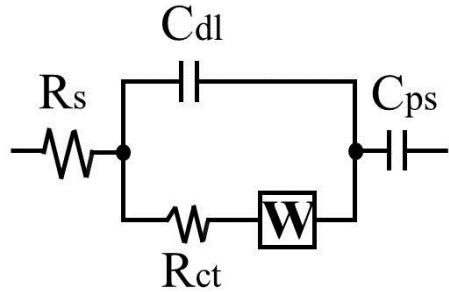


Figure S8. The equivalent circuit mode for the Nyquist plots of NF@CoO, NF@CoO@ZIF-67 and NF@CoO@Co/N-C.

The equivalent circuit for the Nyquist plots of the samples is shown in Figure S8. The semicircle and linear region indicate the charge-transfer resistance (R_{ct}) and Warburg impedance (W), which indicates ion diffusion/transport from the electrolyte to the electrode surface. The intercept with the real axis (Z_{Re}) at high frequency indicates electrolyte resistance (R_s). C_{dl} is the double layer capacitance and C_{ps} is the pseudocapacitance.

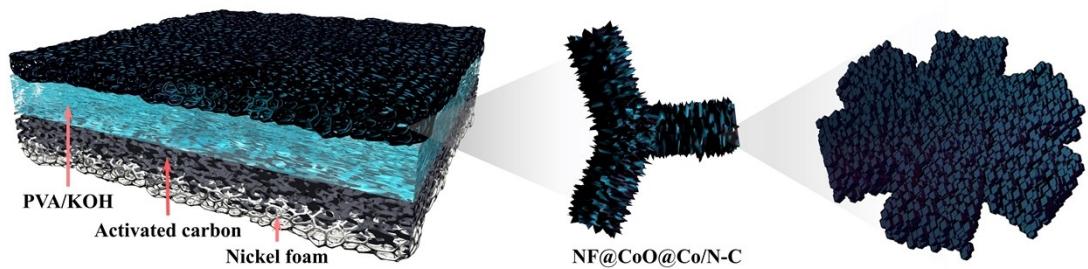


Figure S9. Schematic representation of the ASC device by using NF@CoO@Co/N-C cathode, activated carbon (AC) anode, and PVA/KOH gel as electrolyte.

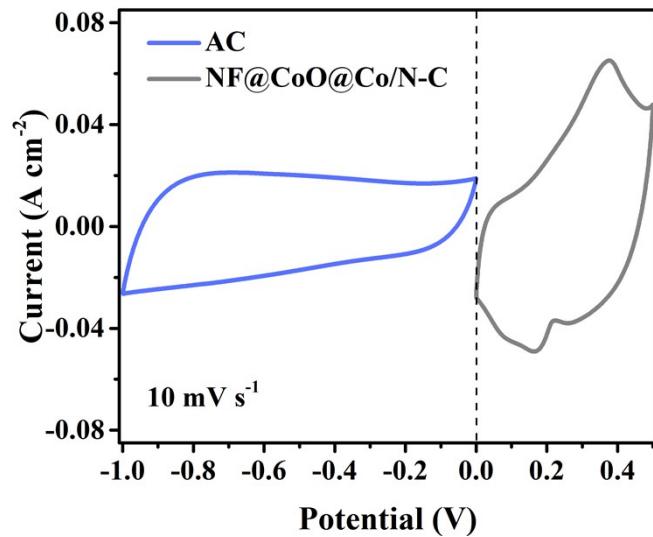


Figure S10. CV curves collected for NF@CoO@Co/N-C and AC electrodes at a scan rate of 10 mV s^{-1} .

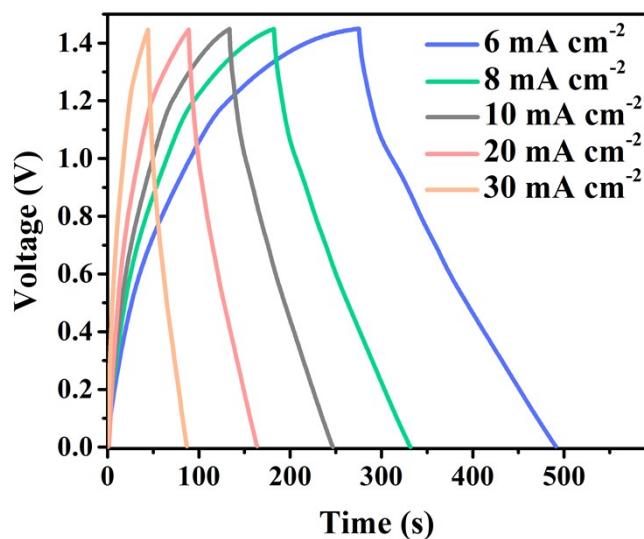


Figure S11. GCD curves of the ASC device at different current densities.

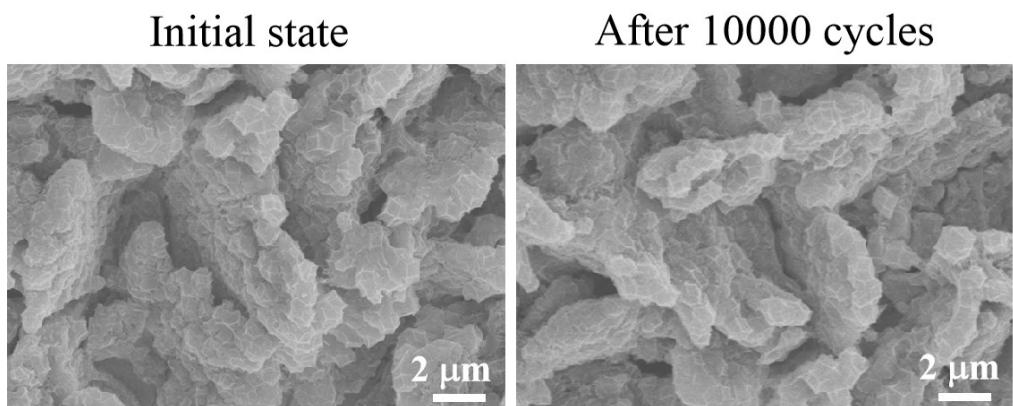


Figure S12. SEM images of NF@CoO@Co/N-C before and after 10000 cycles.

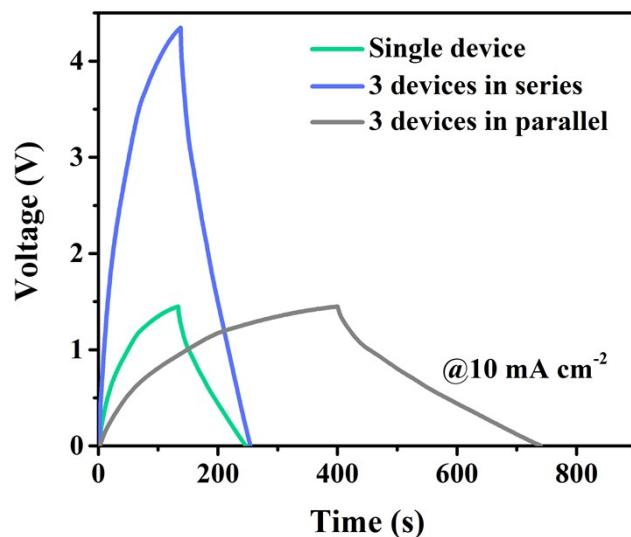


Figure S13. GCD curves of the ASC devices connected in series and in parallel.

Supporting references

- (1) C. Zheng, C. B. Cao, Z. Ali, J. H. Hou, *J. Mater. Chem. A*, 2014, **2**, 16467-16473.
- (2) E. Duraisamy, H. T. Das, A. S. Sharma, P. Elumalai, *New J. Chem.*, 2018, **42**, 6114-6124.
- (3) J. C. Deng, L. T. Kang, G. L. Bai, Y. Li, P. Y. Li, X. G. Liu, Y. Z. Yang, F. Gao, W. Liang, *Electrochimica Acta*, 2017, **132**, 127-135.
- (4) D. Y. Xu, C. P. Mu, J. Y. Xiang, F. S. Wen, C. Su, C. X. Hao, W. T. Hu, Y. F. Tang, Z. Y. Liu, *Electrochimica Acta*, 2016, **220**, 322-330.
- (5) C. Shi, M. W. Chen, X. Han, Y. F. Bi, L. L. Huang, K. Zhou, Z. P. Zheng, *Inorg. Cherm. Front.*, 2018, **5**, 1329-1335.
- (6) X. Ji, S. Cheng, L. F. Yang, Y. Jiang, Z. J. Jiang, C. H. Yang, H. Zhang, M. L. Liu, *Nano Energy*, 2015, **11**, 736-745.
- (7) N. Tang, W. Wang, H. H. You, Z. J. Zhai, J. Hilario, L. Zeng, L. Zhang, *Catal. Today*.
<https://doi.org/10.1016/j.cattod.2018.03.024>
- (8) X. Z. Wang, Y. H. Xiao, D. C. Su, S. G. Xu, L. M. Zhou, S. D. Wu, L. F. Han, S. M. Fang, S. K. Cao, 2016, *Int. J. Hydrogen Energy*, 2016, **41**, 13540-13548.
- (9) J. Y. Long, Z. S. Yan, Y. Gong, J. H. Lin, *Appl. Surf. Sci.*, 2018, **448**, 50-63.
- (10) X. Z. Wang, Y. H. Xiao, D. C. Su, L. M. Zhou, S. D. Wu, L. F. Han, S. M. Fang, S. K. Cao, *Electrochimica Acta*, 2016, **194**, 377-384.